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(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY AND ELECTROLYTE USED FOR THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte secondary battery of excellent charging and discharging efficiency and preservation property even at a high temperature.

SOLUTION: This nonaqueous electrolyte secondary battery is composed of at least a negative electrode containing Li, a Li alloy or material that can store and release Li; a positive electrode containing the material that can store and release Li; and an electrolyte with Li salt dissolved in a nonaqueous solvent. The nonaqueous solvent contains a lactone compound in which fluorine atoms are substituted for one or more hydrogen atoms bonded to carbon atoms constituting a lactone ring, at 0.01-10 wt.% of electrolyte weight.

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CLAIMS

[Claim(s)]

[Claim 1] The negative electrode which contains occlusion and the ingredient which can be emitted for a metal lithium, a lithium alloy, or a lithium, In the nonaqueous electrolyte rechargeable battery which consists of a positive electrode which contains occlusion and the ingredient which can be emitted for a lithium, and the electrolytic solution which comes to dissolve lithium salt in a non-aqueous solvent at least The nonaqueous electrolyte rechargeable battery characterized by the electrolytic-solution weight contained in a nonaqueous electrolyte rechargeable battery containing the lactone compound with which the hydrogen atom combined with the carbon atom which constitutes a lactone ring in said non-aqueous solvent was permuted by or more 1 fluorine atom 0.01 to 10% of the weight.

[Claim 2] The rechargeable battery according to claim 1 characterized by being one or more sorts chosen from the group which the lactone compound with which the hydrogen atom combined with the carbon atom which constitutes a lactone ring was permuted by or more 1 fluorine atom becomes from alpha-fluoro-gamma-butyrolactone and beta-alpha-fluoro-gamma-butyrolactone.

[Claim 3] The rechargeable battery according to claim 1 or 2 which is more than 70 capacity % of said non-aqueous-solvent whole quantity about one or more sorts as which a non-aqueous solvent is chosen from lactone compound, annular carbonate, and chain-like carbonate, chain-like ether, and chain-like carboxylate with 3-9 total carbon, and is characterized by being one or more sorts chosen from the group which more than 20 capacity % of said non-aqueous-solvent whole quantity becomes from a lactone compound with 3-9 total carbon, and annular carbonate with 3-9 total carbon.

[Claim 4] lithium salt -- LiPF6 and LiBF4 from -- the inorganic lithium salt and LiCF3 SO3 which are chosen -- LiN (CF3 SO2)2 and LiN (CF3 CF2 SO2)2, LiN (CF3 SO2) (C4 F9 SO2) and LiPF3 3 (C2F5), LiBF2 2 (CF3) and LiBF2 2 (C two F5) from -- rechargeable battery according to claim 1 to 3 characterized by being one or more sorts of the organic lithium salt chosen from the becoming group.

[Claim 5] The rechargeable battery according to claim 1 to 4 characterized by being that in which occlusion and the ingredient which can be emitted contain the carbonaceous object whose d value of a lattice plane (002) side [in / for the lithium which constitutes a negative electrode / an X diffraction] is 0.335-0.34nm.

[Claim 6] The electrolytic solution used for a nonaqueous electrolyte rechargeable battery according to claim 1 to 5.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the electrolytic solution used for a nonaqueous electrolyte rechargeable battery and it. In detail, by using a specific nonaqueous electrolyte, this invention raises charge-and-discharge effectiveness, and offers the nonaqueous electrolyte rechargeable battery which excelled [bottom / of an elevated temperature] in charge-and-discharge effectiveness and a maintenance property.

[0002]

[Description of the Prior Art] development of the lithium secondary battery which has a high energy density with lightweight-izing of an electric product in recent years, and a miniaturization -- before -- furthermore, it is wished and the improvement of a cell property is also demanded with expansion of Field of application of a lithium secondary battery. current and a positive electrode -- LiCoO₂, LiMnO₂, and LiNiO₂ etc. -- the nonaqueous electrolyte rechargeable battery using occlusion and the compound which can be emitted is proposed by the negative electrode in a lithium ion called metallic-oxide ingredients, such as carbonaceous ingredients, such as corks besides a metal lithium, an artificial graphite, and a natural graphite, and Sn, Si, in a metallic-oxide salt.

[0003] however, in these lithium secondary batteries, a large and small difference should have disassembly of the solvent of the electrolytic solution in an electrode surface on a positive electrode and/or a negative electrode -- happening is known and this causes [of charge-and-discharge effectiveness or a maintenance property] a fall. When the nonaqueous electrolyte rechargeable battery which was independent about the various electrode material of a graphite system, or mixed the lithium with occlusion and other negative-electrode material which can be emitted, and was used as the negative electrode was taken for the example and the electrolytic solution which uses as the main solvent the propylene carbonate used with a lithium primary cell, being fond generally is used, the decomposition reaction of a solvent advances violently on a graphite-electrode front face, and the occlusion of the smooth lithium to a graphite electrode and emission become impossible. On the other hand, since there is little such decomposition, ethylene carbonate is used abundantly as a main solvent of the electrolytic solution of a nonaqueous electrolyte rechargeable battery. However, about ethylene carbonate, in order that the electrolytic solution might cause [in / as a main solvent / a charge-and-discharge process] small quantity [every] decomposition in an electrode surface, there was a problem from which the fall of decline in charge-and-discharge effectiveness etc. takes place.

[0004]

[Problem(s) to be Solved by the Invention] This invention suppresses disassembly of the electrolytic solution of a nonaqueous electrolyte rechargeable battery to the minimum, and charge-and-discharge effectiveness is high and it aims at offering the nonaqueous

electrolyte rechargeable battery of the high energy consistency which excelled [bottom / of an elevated temperature] in the preservation property. In this invention, it is presumed that the protective film with sufficient stability is generated with lithium ion permeability on a positive electrode and/or a negative electrode.

[0005]

[Means for Solving the Problem] In order that this invention person etc. may attain the above-mentioned purpose, as a result of repeating various examination, as the electrolytic solution of a nonaqueous electrolyte rechargeable battery By using the electrolytic solution which contains the lactone compound with which the or more 1 fluorine atom permutation of the hydrogen atom combined with the carbon atom which constitutes a lactone ring was carried out in the range of the amount of specification In order for a coat with sufficient stability to generate efficiently with lithium ion permeability on a positive electrode and/or a negative-electrode front face from the time of early charge and to control disassembly of too much electrolytic solution, it finds out raising charge-and-discharge effectiveness and a preservation property, and came to complete this invention.

[0006] Namely, the negative electrode with which this invention contains occlusion and the ingredient which can be emitted for a metal lithium, a lithium alloy, or a lithium, In the nonaqueous electrolyte rechargeable battery which consists of a positive electrode which contains occlusion and the ingredient which can be emitted for a lithium, and the electrolytic solution which comes to dissolve lithium salt in a non-aqueous solvent at least The lactone compound with which the hydrogen atom combined with the carbon atom which constitutes a lactone ring in said non-aqueous solvent was permuted by or more 1 fluorine atom The electrolytic solution used for the nonaqueous electrolyte rechargeable battery characterized by containing 0.01 to 10% of the weight and it of the electrolytic-solution weight contained in a nonaqueous electrolyte rechargeable battery is offered.

[0007]

[Embodiment of the Invention] As a non-aqueous solvent which can be used for this invention, annular carbonate, chain-like carbonate, lactone compounds (cyclic ester), chain-like ester, cyclic ether, chain-like ether, a sulfur-containing organic solvent, etc. are mentioned. These solvents may be used independently, or two or more kinds may be mixed and they may be used. The numbers of total carbon are the annular carbonate of 3-9, a lactone compound, chain-like carbonate, a carbonate, and chain-like ether preferably in these, respectively. The following is mentioned as an example of the annular carbonate whose numbers of total carbon are 3-9, respectively, a lactone compound, chain-like carbonate, a carbonate, and chain-like ether.

[0008] 1) 3-9 have the annular number of total carbon -- carbonate:ethylene carbonate, propylene carbonate, butylene carbonate, vinylene carbonate, vinyl ethylene carbonate, etc. are mentioned. In this, ethylene carbonate and propylene carbonate are more desirable.

2) the number of total carbon -- lactone compound [of 3-9]: -- gamma-butyrolactone, gamma-valerolactone, delta-valerolactone, etc. can be mentioned and gamma-butyrolactone is more desirable in these.

[0009] 3) the number of total carbon -- chain-like carbonate [of 3-9]: -- dimethyl carbonate -- Dithyl carbonate, G n-propyl carbonate, diisopropyl carbonate, n-propyl isopropyl carbonate, di-n-butyl carbonate, Diisopropyl carbonate, G t-butyl carbonate, n-

butyl isobutyl carbonate, n-butyl-t-butyl carbonate, isobutyl-t-butyl carbonate, Ethyl methyl carbonate, methyl-n-propyl carbonate, n-butyl methyl carbonate, Isobutyl methyl carbonate, t-butyl methyl carbonate, ethyl-n-propyl carbonate, n-butyl ethyl carbonate, isobutyl ethyl carbonate, t-butyl ethyl carbonate, n-butyl-n-propyl carbonate, isobutyl-n-propyl carbonate, t-butyl-n-propyl carbonate, n-butyl isopropyl carbonate, isobutyl isopropyl carbonate, t-butyl isopropyl carbonate, etc. can be mentioned. In these, dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate are desirable.

[0010] 4) A carbonate with 3-9 total carbon : methyl acetate, ethyl acetate, n propyl acetate, acetic-acid-isopropyl, n-butyl acetate, isobutyl acetate, acetic-acid-t-butyl, methyl propionate, ethyl propionate, propionic-acid-n-propyl, propionic-acid-isopropyl, propionic-acid-n-butyl, propionic-acid isobutyl, and propionic-acid-t-butyl can be mentioned. In these, ethyl acetate, methyl propionate, and ethyl propionate are still more desirable.

[0011] 5) The chain-like ether with 3-6 total carbon : dimethoxymethane, dimethoxyethane, diethoxy methane, diethoxy ethane, ethoxy methoxy methane, ethoxy methoxyethane, etc. can be mentioned. In these, dimethoxyethane and diethoxy ethane are more desirable. In this invention, the non-aqueous solvent in the electrolytic solution contained in a nonaqueous electrolyte rechargeable battery Lactone compound [with 3-9 total carbon], annular carbonate, and chain-like carbonate, It is more than 70 capacity % of said non-aqueous-solvent whole quantity about one or more sorts chosen from chain-like ether and chain-like carboxylate. And it is desirable that they are one or more sorts chosen from the group which more than 20 capacity % of said non-aqueous-solvent whole quantity becomes from a lactone compound with 3-9 total carbon and annular carbonate with 3-9 total carbon.

[0012] Lithium salt is used as a solute of the electrolytic solution used by this invention. About lithium salt, if it can be used as a solute, especially limitation will not be carried out. As the example, for example, 1 inorganic lithium salt:LiPF6 and LiAsF6, LiBF4, the inorganic fluoride salt of LiAlF4 grade, and LiClO4, LiBrO4 and LiIO4 etc. -- fault halogen acid salt 2 organic lithium salt: -- LiCF3 SO3 etc. -- an organic sulfonate -- LiN (CF3 SO2)2 and LiN (C2 F5 SO2)2, Perfluoroalkyl sulfonic-acid imide salts, such as LiN (CF3 SO2) (C4 F9 SO2), LiC (CF3 SO2)3 etc. -- a perfluoroalkyl sulfonic-acid methide salt -- LiPF (CF3)5, LiPF2 4 (CF3), and LiPF3 3 (CF3), LiPF2 4 (C two F5) and LiPF3 3 (C two F5), LiPF (n-C three F7)5 and LiPF2 4 (n-C three F7), LiPF3 3 (n-C three F7) and LiPF (iso-C three F7)5, LiPF2 4 (iso-C three F7) and LiPF3 3 (iso-C three F7), LiB (CF3)4, LiBF (CF3)3, and LiBF2 2 (CF3), LiBF3 (CF3), LiB (C2F5)4, and LiBF (C two F5)3, LiBF2(C two F5) 2 and LiBF3 (C two F5), LiB (n-C three F7)4 and LiBF (n-C three F7)3, LiBF2 2 (n-C three F7) and LiBF3 (n-C3F7), LiB (iso-C three F7)4 and LiBF (iso-C three F7)3, The inorganic fluoride salt fluoro phosphate which permuted some (iso-C three F7) fluorines of LiBF2 2 (iso-C three F7), LiBF3, etc. by the perfluoroalkyl radical, and the fluorine-containing organic lithium salt of perfluoroalkyl are mentioned. The inside of these, LiPF6 and LiBF4, and LiN (CF3 SO2)2, LiN (C2 F5 SO2)2, LiN (CF3 SO2) (C4 F9 SO2), LiPF3 3 (CF3), LiPF3 3 (C two F5), and LiBF2 2 (C two F5) It is more desirable.

[0013] In addition, two or more kinds may be mixed and these solutes may be used. As for the lithium salt mol concentration of the solute in the electrolytic solution, it is desirable that it is 0.5-3 mols/l. If concentration is too low, the conductivity of the

electrolytic solution is inadequate by absolute low density, and if concentration is too deep, since conductivity will fall since it is a viscosity rise and a deposit at low temperature will become easy to take place, the engine performance of a cell falls and is not desirable.

[0014] In the non-aqueous solvent of the electrolytic solution used for this invention, it may not be characterized by containing the lactone compound with which the or more 1 fluorine atom permutation of the hydrogen atom combined with the carbon atom which constitutes a lactone ring was carried out, and you may have the substituent in the range which does not check the expected effectiveness of this invention too much. Specifically alpha-fluoro-gamma-butyrolactone, beta-fluoro-gamma-butyrolactone, gamma-fluoro-gamma-butyrolactone, alpha, and alpha-difluoro-gamma-butyrolactone, alpha, beta-difluoro-gamma-butyrolactone, alpha, gamma-difluoro-gamma-butyrolactone, beta and beta-difluoro-gamma-butyrolactone, beta, gamma-difluoro-gamma-butyrolactone, gamma and gamma-difluoro-gamma-butyrolactone, alpha and alpha, beta-trifluoro-gamma-butyrolactone, alpha, beta, and beta-trifluoro-gamma-butyrolactone, alpha and alpha, gamma-trifluoro-gamma-butyrolactone, alpha, beta, gamma-trifluoro-gamma-butyrolactone, alpha and gamma, gamma-trifluoro-gamma-butyrolactone, beta, beta, gamma-trifluoro-gamma-butyrolactone, beta and gamma, gamma-trifluoro-gamma-butyrolactone, alpha, alpha, beta, and beta-tetrafluoro-gamma-butyrolactone, alpha, alpha, beta, gamma-tetrafluoro-gamma-butyrolactone, alpha and alpha, gamma-gamma-tetrafluoro-gamma-butyrolactone, alpha, beta, gamma-tetrafluoro-gamma-butyrolactone, beta, beta and gamma, gamma-tetrafluoro-gamma-butyrolactone, alpha, alpha, beta, beta, gamma-pentafluoro-gamma-butyrolactone, alpha, alpha, beta and gamma, gamma-pentafluoro-gamma-butyrolactone, hexafluoro-gamma-butyrolactone, [0015] An alpha-fluoro-delta-valerolactone, a beta-fluoro-delta-valerolactone, A gamma-fluoro-delta-valerolactone, a delta-fluoro-delta-valerolactone, An alpha and alpha-difluoro-delta-valerolactone, alpha, a beta-difluoro-delta-valerolactone, alpha, gamma-difluoro-gamma-butyrolactone, alpha, delta-difluoro-gamma-butyrolactone, A beta and beta-difluoro-delta-valerolactone, beta, a gamma-difluoro-delta-valerolactone, A beta, delta-difluoro-delta-valerolactone, gamma, and gamma-difluoro-delta-valerolactone, gamma, delta-difluoro-delta-valerolactone, delta, and delta-difluoro-delta-valerolactone, [0016] An alpha, alpha, beta-trifluoro-delta-valerolactone, alpha and beta, and beta-trifluoro-delta-valerolactone, alpha, alpha, a gamma-trifluoro-delta-valerolactone, alpha and beta, a gamma-trifluoro-delta-valerolactone, An alpha, gamma, and gamma-trifluoro-delta-valerolactone, alpha and beta, a delta-trifluoro-delta-valerolactone, An alpha, gamma, delta-trifluoro-delta-valerolactone, alpha and delta, and delta-trifluoro-delta-valerolactone, beta, beta, a gamma-trifluoro-delta-valerolactone, beta and beta, a delta-trifluoro-delta-valerolactone, A beta, gamma, and gamma-trifluoro-delta-valerolactone, beta and gamma, a delta-trifluoro-delta-valerolactone, A beta, delta, and delta-trifluoro-delta-valerolactone, gamma and gamma, delta-trifluoro-delta-valerolactone, gamma and delta, and delta-trifluoro-delta-valerolactone, [0017] An alpha, alpha, beta, and beta-tetrafluoro-delta-valerolactone, alpha, alpha, beta, A gamma-tetrafluoro-delta-valerolactone, alpha, alpha and beta, a delta-tetrafluoro-delta-valerolactone, An alpha, alpha, gamma, and gamma-tetrafluoro-delta-valerolactone, alpha, alpha, gamma, A delta-tetrafluoro-delta-

valerolactone, alpha, alpha and delta, and delta-tetrafluoro-delta-valerolactone, alpha, beta, beta, a gamma-tetrafluoro-delta-valerolactone, alpha, beta, beta, A delta-tetrafluoro-delta-valerolactone, alpha, beta and gamma, and gamma-tetrafluoro-delta-valerolactone, alpha, beta, gamma, a delta-tetrafluoro-delta-valerolactone, alpha, beta, delta, A delta-tetrafluoro-delta-valerolactone, beta, beta and gamma, and gamma-tetrafluoro-delta-valerolactone, A beta, beta, gamma, delta-tetrafluoro-delta-valerolactone, beta, beta and delta, and delta-tetrafluoro-delta-valerolactone, gamma, gamma and delta, and delta-tetrafluoro-delta-valerolactone, [0018] alpha, alpha, beta, beta, a gamma-pentafluoro-delta-valerolactone, alpha, alpha, beta, beta, a delta-pentafluoro-delta-valerolactone, alpha, alpha, beta, gamma. A gamma-pentafluoro-delta-valerolactone, alpha, alpha, beta, delta, and delta-pentafluoro-delta-valerolactone, alpha, beta, A beta, gamma, and gamma-pentafluoro-delta-valerolactone, alpha, beta, beta, gamma, A delta-pentafluoro-delta-valerolactone, alpha, beta, beta and delta, and delta-pentafluoro-delta-valerolactone, alpha, beta, gamma, gamma, a delta-pentafluoro-delta-valerolactone, alpha, beta, A gamma, delta, and delta-pentafluoro-delta-valerolactone, beta, beta, gamma and gamma, delta-pentafluoro-delta-valerolactone, beta, beta, gamma and delta, and delta-pentafluoro-delta-valerolactone, beta, gamma, gamma and delta, and delta-pentafluoro-delta-valerolactone, [0019] An alpha, alpha, beta, beta, gamma, and gamma-hexafluoro-delta-valerolactone, alpha, alpha, beta, beta and gamma, delta-HEKI A SAFURUORO-delta-valerolactone, alpha, alpha, beta, beta and delta, and delta-hexafluoro-delta-valerolactone, alpha, alpha, beta, gamma, delta-hexafluoro-delta-valerolactone, alpha, beta, beta, gamma, gamma, a delta-hexafluoro-delta-valerolactone, alpha, beta, beta, A gamma, delta, and delta-hexafluoro-delta-valerolactone, alpha, beta, gamma, gamma, A delta and delta-hexafluoro-delta-valerolactone, alpha, alpha, beta, beta, gamma, gamma, a delta-heptafluoro-delta-valerolactone, alpha, alpha, beta, beta, gamma, A delta and delta-heptafluoro-delta-valerolactone, alpha, alpha, beta, gamma, gamma and delta, and delta-heptafluoro-delta-valerolactone, alpha, beta, beta, gamma, gamma and delta, and delta-heptafluoro-delta-valerolactone, an octafluoro-delta-valerolactone, [0020] A 2-fluoro-gamma-valerolactone, a 3-fluoro-gamma-valerolactone, A 4-fluoro-gamma-valerolactone, 2, and 2-difluoro-gamma-valerolactone, A 2, 3-difluoro-gamma-valerolactone, 3, and 3-difluoro-gamma-valerolactone, 3, a 4-difluoro-gamma-valerolactone, 2 and 2, a 3-trifluoro-gamma-valerolactone, A 2, 3, and 3-trifluoro-gamma-valerolactone, 2 and 2, a 4-trifluoro-gamma-valerolactone, A 3, 3, 4-trifluoro-gamma-valerolactone, 2, 2 and 3, and 3-tetrafluoro-gamma-valerolactone, A 2, 2, 3, 4-tetrafluoro-gamma-valerolactone, 2, 3 and 3, 4-tetrafluoro-gamma-valerolactone, 2, 2, 3 and 3, and 4-pentafluoro-gamma-valerolactone is mentioned.

[0021] A lactone compound will tend to become unstable if too much fluorination is performed, and separation with manufacture and an isomer also changes difficult, furthermore, from becoming easy to cause the fall of solubility, although separation with an isomer becomes unnecessary if it perfluoro-izes alpha-fluoro-gamma-butyrolactone, beta-fluoro-gamma-butyrolactone, gamma-fluoro-gamma-butyrolactone, an alpha-fluoro-delta-valerolactone, A beta-fluoro-delta-valerolactone, a gamma-fluoro-delta-valerolactone, A delta-fluoro-delta-valerolactone, a 2-fluoro-gamma-valerolactone, Mono-fluoro lactone, such as a 3-fluoro-gamma-valerolactone and a 4-fluoro-gamma-

valerolactone, is more desirable still more desirable, and alpha-fluoro-gamma-butyrolactone and beta-fluoro-gamma-butyrolactone are more desirable.

[0022] Two or more kinds may be mixed and these may be used, without separating an isomer with difficult separation. Moreover, it may mix with the well-known compound which can be added to the electrolytic solution of a lithium secondary battery, and you may use. Moreover, based on the electrolytic-solution weight contained in a rechargeable battery, 0.01 - 10 % of the weight of loadings is desirable, and its 0.1 - 6 % of the weight is more desirable.

[0023] If it separates from the above-mentioned range, it is not a desirable thing that cell properties, such as charge-and-discharge effectiveness and a preservation property, fall etc. Although a lithium will not be limited as an ingredient of the negative electrode which constitutes the cell of this invention especially if occlusion and the ingredient which may be emitted are included, as the example, the carbon material [, such as a pyrolysis object of the organic substance in various pyrolysis conditions, and an artificial graphite, a natural graphite,], metallic-oxide ingredient, and lithium alloy of versatility [list / lithium metal] further is mentioned, for example.

[0024] It is the ingredient which performed various surface treatment which contains a pitch in the artificial graphite manufactured by elevated-temperature heat treatment of the easy graphite pitch obtained from various raw materials desirable as a carbon material among these and purification natural graphites, or these graphites. These carbon materials have that desirable 0.335-0.34nm (distance between layers) of whose d values of the lattice plane (002) side searched for by the X diffraction by Gakushin method is 0.335-0.337nm more preferably. As for these carbon materials, it is desirable that the microcrystal size (Lc) for which ash content is 0.1 or less % of the weight, and asked by the X diffraction by Gakushin method 0.5 or less % of the weight more preferably 1 or less % of the weight is 30nm or more. Furthermore, 50nm or more of microcrystal size (Lc) is more more desirable, and what is 100nm or more is the most desirable. Moreover, a median size is a median size by the method of laser diffracting / being scattered about, and is 7 micrometers - 30 micrometers still more preferably 5 micrometers - 40 micrometers more preferably 3 micrometers - 50 micrometers 1 micrometer - 100 micrometers. moreover, BET adsorption method specific surface area -- 0.5m² / g-25.0m² / g -- it is -- desirable -- 0.5m² / g-20.0m² / g -- more -- desirable -- 0.6m² / g-15.0m² / g -- they are 0.6m² / g-10.0m² / g still more preferably. Moreover, it sets to the Raman spectrum analysis using Ar-ion-laser light, and they are intensity ratio R=IB of Peak PA and (peak intensity IA) the peak PB (peak intensity IB) of the range of 1350-1370cm⁻¹ / IA to the range of 1580-1620cm⁻¹. 1 or less [26cm⁻¹] and 1 or less [25 morecm⁻¹] have the more desirable full width at half maximum of the range of zero to 0.5, and 1580-1620cm⁻¹.

[0025] Moreover, the metallic compounds which emit [occlusion and] a lithium can also be mixed and used for these carbonaceous ingredients. As metallic compounds which emit [occlusion and] lithiums other than a carbonaceous ingredient, although metals, such as Ag, Zn, aluminum, Ga, In, Si, germanium, Sn, Pb, P, Sb, Bi, Cu, nickel, Sr, and Ba, the alloy of Li or the metallic-oxide ingredient of these metals, and a lithium metal are mentioned, Sn oxide, Si oxide, aluminum oxide, the lithium alloy of Sn, Si, and aluminum, and a metal lithium are mentioned preferably.

[0026] Two or more kinds may be mixed and these negative-electrode ingredients may be

used. Especially the method of manufacturing a negative electrode using these negative-electrode ingredients is not limited. For example, it can apply to the substrate of a charge collector, and by drying, a negative electrode can be manufactured and roll forming of this negative-electrode ingredient is carried out as it is, and a binder, a thickener, electric conduction material, a solvent, etc. can be added to a negative-electrode ingredient if needed, and it can consider as the shape of a slurry, and can also consider [it can consider as a sheet electrode or] as a pellet electrode with compression molding.

[0027] When using a binder for manufacture of an electrode, if it is a stable ingredient, it will not be especially limited to the solvent used at the time of electrode manufacture, the electrolytic solution, and other ingredients used at the time of cell use. As the example, polyvinylidene fluoride, polytetrafluoroethylene, styrene-butadiene rubber, polyisoprene rubber, butadiene rubber, etc. can be mentioned.

[0028] When using a thickener for manufacture of an electrode, if it is a stable ingredient, it will not be especially limited to the solvent used at the time of electrode manufacture, the electrolytic solution, and other ingredients used at the time of cell use. As the example, a carboxymethyl cellulose, methyl cellulose, a hydroxymethyl cellulose, ethyl cellulose, polyvinyl alcohol, oxidization starch, phosphorylation starch, GAZEIN, etc. are mentioned.

[0029] When using electric conduction material for manufacture of an electrode, if it is a stable ingredient, it will not be especially limited to the solvent used at the time of electrode manufacture, the electrolytic solution, and other ingredients used at the time of cell use. As the example, carbon materials, such as metallic materials, such as copper and nickel, graphite, and carbon black, are mentioned. The quality of the material of the charge collector for negative electrodes has the point of metals, such as copper, nickel, and stainless steel, being used and being easy to process it into a thin film in these, and the point of cost to desirable copper foil.

[0030] As an ingredient of the positive electrode which constitutes the cell of this invention, the ingredient which emits [occlusion and] lithiums, such as lithium transition-metals multiple oxide ingredients, such as lithium cobalt oxide, a lithium nickel oxide, and a lithium manganic acid ghost, can be used. Especially about the manufacture approach of a positive electrode, it is not limited but can manufacture according to the manufacture approach of the above-mentioned negative electrode. Moreover, about the configuration, after mixing, a binder, electric conduction material, a solvent, etc. can be added to a positive-electrode ingredient if needed, and it applies to the substrate of a charge collector, and it can consider as a sheet electrode or can consider [press forming can be performed and] as a pellet electrode.

[0031] As for the quality of the material of the charge collector for positive electrodes, metals, such as aluminum, titanium, and a tantalum, or the alloy of those is used. In these, since especially aluminum or its alloy is lightweight, it is desirable in respect of energy density. It is not limited especially about the quality of the material or the configuration of a separator which are used for the cell of this invention. However, it is stable to the electrolytic solution, and choosing from the solution retention outstanding ingredients is desirable, and it is desirable to use a porous sheet or a nonwoven fabric etc. which uses polyolefines, such as polyethylene and polypropylene, as a raw material.

[0032] Especially about the method of manufacturing the cell of this invention which has a negative electrode, a positive electrode, and a nonaqueous electrolyte at least, it is not

limited but can choose suitably from the approaches usually adopted. Moreover, the coin type which carried out the laminating of the cylinder type, pellet electrode, and separator of the inside-out configuration which combined the cylinder type, pellet electrode, and separator which were not limited especially about the configuration of a cell but made the sheet electrode and the separator the shape of a spiral is usable.

[0033]

[Example] Although an example and the example of a comparison are given to below and this invention is explained to it still more concretely, this invention is not limited to these examples, unless the summary is exceeded.

About the electrolytic solution, the hoc lithium fluoride (LiBF4) which fully dried is used as a solute under desiccation argon atmosphere. (Example 1) Use gamma-butyrolactone as a non-aqueous solvent, and alpha-fluoro-gamma-butyrolactone is dissolved at 5% of the weight of a rate based on electrolytic-solution weight. Moreover, LiBF4 It dissolved and prepared at a rate of one mol/l., the coin mold cel was produced by the after-mentioned approach, and it evaluated about initial charge-and-discharge effectiveness and a preservation property. A result is shown in Table 1.

[0034] (Example 2) It replaced with alpha-fluoro-gamma-butyrolactone and evaluated like the example 1 except having dissolved beta-fluoro-gamma-butyrolactone at 5% of the weight of a rate.

(Example 3) It replaced with alpha-fluoro-gamma-butyrolactone and evaluated like the example 1 except having dissolved the mixture of 1:1 of alpha-fluoro-gamma-butyrolactone and beta-fluoro-gamma-butyrolactone at 5% of the weight of a rate.

[0035] (Example 4) It replaced with alpha-fluoro-gamma-butyrolactone and evaluated like the example 1 except having dissolved the alpha-fluoro-gamma-valerolactone at 5% of the weight of a rate.

(Example 5) It replaced with alpha-fluoro-gamma-butyrolactone and evaluated like the example 1 except having dissolved the alpha-fluoro-delta-valerolactone at 5% of the weight of a rate.

[0036] (Example 6) Propylene carbonate is used as a non-aqueous solvent, alpha-fluoro-gamma-butyrolactone is dissolved at 5% of the weight of a rate, and it is LiPF6 further. It evaluated like the example 1 except having considered as the electrolytic solution dissolved and prepared at a rate of one mol/l.

[0037] (Example 7) Propylene carbonate is used as a non-aqueous solvent, beta-fluoro-gamma-butyrolactone is dissolved at 5% of the weight of a rate, and it is LiPF6 further. It evaluated like the example 1 except having considered as the electrolytic solution dissolved and prepared at a rate of one mol/l.

[0038] (Example 8) Propylene carbonate is used as a non-aqueous solvent, the mixture of 1:1 of alpha-fluoro-gamma-butyrolactone and beta-fluoro-gamma-butyrolactone is dissolved at 5% of the weight of a rate, and it is LiPF6 further. It evaluated like the example 1 except having considered as the electrolytic solution dissolved and prepared at a rate of one mol/l.

[0039] (Example 9) Propylene carbonate is used as a non-aqueous solvent, alpha-fluoro-gamma-butyrolactone is dissolved at 5% of the weight of a rate, and it is LiPF6 further. It evaluated like the example 1 except having considered as the electrolytic solution dissolved and prepared at a rate of one mol/l.

[0040] (Example 10) Propylene carbonate is used as a non-aqueous solvent, an alpha-

fluoro-delta-valerolactone is dissolved at 5% of the weight of a rate, and it is LiPF6 further. It evaluated like the example 1 except having considered as the electrolytic solution dissolved and prepared at a rate of one mol/l.

[0041] (Example 1 of a comparison) It is LiBF4, without other things adding to the gamma-butyrolactone as a non-aqueous solvent. It evaluated like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of one mol/l.

(Example 2 of a comparison) Propylene carbonate is used as a non-aqueous solvent, and it is LiPF6 to this. It evaluated like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of one mol/l.

[0042] (Production of a positive electrode) It is LiCoO2 as positive active material. 6 % of the weight of carbon black and polyvinylidene fluoride KF-1000(Kureha chemistry company make, trade name) 9 % of the weight were added to 85% of the weight, and it mixed, and distributed by the N-methyl-2-pyrrolidone, and what was made into the shape of a slurry was applied to homogeneity on aluminium foil with a thickness of 20 micrometers which is a positive-electrode charge collector, and after desiccation, it pierced to discoid with a diameter of 12.5mm, and considered as the positive electrode.

[0043] d value of the lattice plane (002) side in an X diffraction 0.336nm, (Creation of a negative electrode) 100nm or more (264nm) and ash content 0.04 % of the weight, [crystallite size (Lc)] 17 micrometers and BET adsorption method specific surface area 8.9m2 / g, [the median size by the method of laser diffracting / being scattered about] In the Raman spectrum analysis using Ar-ion-laser light The peak PA of the range of 1580-1620cm-1 (Peak intensity IA) artificial-graphite powder KS-44 [and] (the TIMCAL, LTD. make --) whose full width at half maximum of the range of 0.15 and 1580-1620cm-1 intensity ratio R=IB of the peak PB (peak intensity IB) of the range of 1350-1370cm-1 / IA is 22.2cm-1 In addition, the styrene butadiene rubber (SBR) which 94 % of the weight of trade names was made to distribute with distilled water is mixed by the De Dis parser so that it may become 6 % of the weight by solid content. What was made into the shape of a slurry was applied to homogeneity on copper foil with a thickness of 18 micrometers which is a negative-electrode charge collector, and after desiccation, it pierced to discoid with a diameter of 12.5mm, the electrode was produced, and it used as a negative electrode.

[0044] (Production of a coin mold cel) The positive electrode was held in the can made from stainless steel which serves as a positive-electrode conductor using the above-mentioned positive electrode, a negative electrode, and the electrolytic solution, and the negative electrode was laid through the separator made from polyethylene which infiltrated the electrolytic solution on it. the obturation plate which serves both as this can and a negative-electrode conductor -- the gasket for an insulation -- minding -- it sealed in total and the coin mold cel was produced.

[0045] (Evaluation of a coin mold cel) In 25 degrees C, the value which performed the charge and discharge test according to 0.5mA constant current by charge termination electrical-potential-difference 4.2V and discharge-final-voltage 2.5V, and broke the discharge capacity of a two-cycle eye by charge capacity of a two-cycle eye was defined as two-cycle eye charge-and-discharge effectiveness. Moreover, after charging on the same conditions after a four cycle and saving at 85 degrees C in the state of charge for 72 hours, it was made to discharge and, subsequently charge and discharge of 5 cycle eye were performed. The value which broke the discharge capacity of this 5 cycle eye by

charge capacity of 5 cycle eye was defined as the preservation property.

[0046]

[Effect of the Invention] The nonaqueous electrolyte rechargeable battery charge-and-discharge effectiveness and whose preservation property improved can be offered by using the electrolytic solution which carried out the amount combination of specification of the lactone compound with which the or more 1 fluorine atom permutation of the hydrogen atom combined with the carbon atom which constitutes a lactone ring in a non-aqueous solvent was carried out.

[0047]

[Table 1]

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[Translation done.]
